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☐ 1. Document ID: US 6342389 B1

L3: Entry 1 of 3

File: USPT

Jan 29, 2002

US-PAT-NO: 6342389

DOCUMENT-IDENTIFIER: US 6342389 B1

TITLE: Modified phycobilisomes and uses therefore

DATE-ISSUED: January 29, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cubicciotti; Roger S.	Montclair	NJ	07042	

US-CL-CURRENT: 435/317.1; 435/4, 435/7.1, 435/7.2, 435/7.8, 435/963, 436/518,
436/519, 436/524, 436/527, 436/536, 530/391.3, 530/402

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KNOC	Draw D
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☐ 2. Document ID: US 6022500 A

L3: Entry 2 of 3

File: USPT

Feb 8, 2000

US-PAT-NO: 6022500

DOCUMENT-IDENTIFIER: US 6022500 A

TITLE: Polymer encapsulation and polymer microsphere composites

DATE-ISSUED: February 8, 2000

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
John; Vijay T	Kenner	LA		
McPherson; Gary L	Mandeville	LA		
Akkara; Joseph A	Holliston	MA		
Kaplan; David L	Stow	MA		

US-CL-CURRENT: 264/4.1; 264/4.3, 264/4.33, 264/4.6, 264/4.7, 427/213.3, 427/213.31,
427/213.34, 427/213.36, 427/215

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KNOC	Draw D
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☐ 3. Document ID: US 5770559 A

L3: Entry 3 of 3

File: USPT

Jun 23, 1998

US-PAT-NO: 5770559

DOCUMENT-IDENTIFIER: US 5770559 A

TITLE: Solubilization of pharmaceutical substances in an organic solvent and preparation of pharmaceutical powders using the same

DATE-ISSUED: June 23, 1998

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Manning; Mark C.	Fort Collins	CO		
Randolph; Theodore W.	Niwot	CO		
Shefter; Eli	LaJolla	CA		
Falk, III; Richard F.	Boulder	CO		

US-CL-CURRENT: 514/2; 424/450, 424/489, 514/21, 530/412, 530/418, 530/419, 530/427

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw D.
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L8: Entry 10 of 12

File: USPT

Sep 2, 1986

DOCUMENT-IDENTIFIER: US 4609444 A

TITLE: Photochemical reactions for commercial synthesis

Abstract Text (1):

Photochemical reactions are conducted using polymer beads arranged as a monolayer, e.g. floating on the surface of a moving body of water. The polymer bead is impregnated with a reactant, floated on the water or otherwise exposed as a monolayer in direct sunlight so as to expose the reactant to solar radiation, collected at a downstream location, treated to remove product from the polymer, and then the bead can be recycled. The process can be used to collect and store solar energy in chemical form, or for conducting photochemical synthesis to produce useful chemical products.

Brief Summary Text (12):

Most suitably, the carrier material is a mass of buoyant beads or discs each comprising a substantially water-insoluble, UV-stable polymer. Thus the carrier may comprise hollow glass spheres coated with a suitable polymer, optionally covered with a protective film of low oxygen permeable polymer, or foam-cored plastic spheres provided with a suitable polymer coating. The water-insoluble, UV-stable polymer is treated, e.g. impregnated, with the reactant material so that it is swollen thereby but does not chemically react with the reactant material. In similar manner the product formed by photochemical reaction of the reactant while impregnated in the polymer, is similarly chemically inert to the chosen polymer and extractable therefrom, but nevertheless remains supported e.g. impregnated in the polymer until positive steps are taken to extract the product from the carrier. The type of polymer is thus chosen in conjunction with the reactants to be used and the products to be formed, with a view to arranging suitable inertness, support and product extractability.

Brief Summary Text (14):

In another preferred embodiment of the invention, the floating carrier material on the body of liquid is covered by a solar radiation permeable but substantially gas impermeable film or membrane. Then a selected gaseous atmosphere can be provided, beneath the film in contact with the reactant material either to supply a reactant thereto or to protect the reactant or products from atmospheric effects e.g. oxygen.

Drawing Description Text (2):

FIG. 1 is a cross-sectional view of a first embodiment of polymer-bearing bead useful in the invention.

Drawing Description Text (3):

FIG. 2 is a cross-sectional view of an alternative form of polymer-bearing bead useful in the invention;

Drawing Description Text (4):

FIG. 3 is a cross-sectional view of a further form of polymer-bearing bead useful in the invention;

Drawing Description Text (5):

FIG. 4 is a top plan view of another form of polymer-bearing bead useful in the invention;

Drawing Description Text (7):

FIG. 6 is a perspective view of a different polymer-bearing bead useful in the invention.

Detailed Description Text (2):

FIG. 1 shows a cross-sectional view of one embodiment of the invention. The bead comprises a glass sphere 22 with a hollow interior 24. The sphere 22 is surrounded by a layer of cross-linked, swellable polymer 20, namely cross-linked polymethylacrylate.

Detailed Description Text (3):

The hollow sphere 22 acts as a buoyant particle surrounded by the swellable polymer layer 20 in which the photo chemically reactive reagents are retained and photochemically react on exposure to solar U.V. radiation.

Detailed Description Text (4):

FIG. 2 illustrates a form of bead suitable for use where the photochemical reactions are inhibited by oxygen. It depicts a basically similar bead as shown in FIG. 1 with glass sphere 22 and hollow interior 24 surrounded by swollen polymer layer 20 in which the photochemically reactive reagent is contained, but also includes an outer thin film 26. Thin film 26 consists of a low oxygen permeability elastomer film that allows reactions to occur in the swollen polymer in the absence of oxygen, while permitting sufficient solar radiation to pass therethrough to reach polymer layer 20.

Detailed Description Text (5):

FIG. 3 shows another form of bead for use in the invention which consists of a spherically shaped bead with inner cross-linked expanded foam core 32 surrounded by a cross-linked polymer layer 30. The foam core 32 which contains air pockets and acts as a buoyant particle, similar to the hollow sphere in FIG. 1 described above, may be made of any polymer stable to solar U.V. radiation for example, polystyrene, polyacrylonitrile or polymethacrylonitrile and is most easily prepared by irradiation of prefoamed polymer beads. Cross-linking of the foam, which is caused by irradiation, must be enough to prevent destruction of the foam when exposed to swelling solvents.

Detailed Description Text (6):

A further useful form of bead, depicted in FIG. 4 and in FIG. 5, is of different shape but is similar in construction to that of FIG. 3. It has a flattened, disk-like shape, i.e. constituting a platelet. FIG. 5 shows the cross-linked foam core 32 which is surrounded by a thin layer 30 of cross-linked polymer. Both the core 32 and polymer layer 30 may be made of the same materials as those described in FIG. 3. The shape of this bead allows for a large area of exposure to solar radiation and thus efficient conversion of the reagents therein.

Detailed Description Text (7):

FIG. 6 depicts another form of bead for use in the invention. The embodiment is a rod shaped bead with an inner core 42 surrounded by a thin polymer layer 40. The core may be made of any foamed or unfoamed low density polymer, for example polyethylene, and the polymer layer 40 may be made of any of a variety of polymers as described herein. Solid, buoyant polymer rods are also useful.

Detailed Description Text (8):

The dimensions of the beads as shown above, will depend on the thickness of the polymer layer which, in turn, depends on the extinction coefficient of reactive materials and their concentration in the polymer layer. Preferred layer thicknesses are in the range of 0.1 mm to 2.0 mm., though greater layer thicknesses are also

suitable.

Detailed Description Text (10):

The process of the invention contemplates the use of buoyant polymer beads, which float on the body of liquid, normally water. The density of the body of water can be increased, if desired, to promote the buoyancy of the beads, by dissolving salts in the water (sodium chloride, calcium chloride etc.). Such salted solar ponds are known. This provides a means by which normally non-water-buoyant polymer beads can be used as the carrier for photochemical reactions.

Detailed Description Text (13):

An embodiment of the process of the invention is illustrated schematically in FIG. 7. This shows a body of water 50 flowing in the direction of arrow A. Polymer-bearing, buoyant beads 52 of one of the types previously described, are fed to an impregnating vessel 54 disposed at an upstream location relative to the body of water for receiving chemical reactant. The reactant is fed to impregnating vessel 54 via inlet 56 and impregnates the beads therein. The impregnated beads are then poured onto the surface of the body of water 50, on which they float and spread out as a monolayer, at the surface of the body of water as illustrated, thereby exposing the reactant impregnated therein to incident solar radiation as indicated. The beads 52 are transported by the moving body of water to a weir arrangement 58 over which the water and beads fall into a screened receiving vessel 60 where the beads, now impregnated with chemical product are separated from the water by screen 62 and fed to a product recovery vessel 64, where the chemical product is separated from the beads, e.g. by solvent extraction, and recovered via exit 66. The beads 52 are then recycled via line 68 for re-impregnation in vessel 54 with reactant and repeat of the cycle.

Detailed Description Text (14):

The polymer for use as the carrier for the reactants and products can be chosen from a wide variety of different polymers, having regard to the function which it is to perform. The polymer must be chosen with regard to its ability to retain the specific reactants and products in a stable but readily recoverable manner, and without chemically reacting or interfering with the reactants, products or course of reaction therein. Organic polymers and organic compounds generally show a reasonable degree of compatibility with one another, with the compounds having a solubility in the polymers, to various extents. The polymer must be stable on exposure to UV and other solar radiations. It must be substantially unaffected by water --where normally water soluble polymers are to be used, they are used in cross-linked form to impart the necessary water resistance. Preferred polymers are capable of repeated cycles of impregnation with reactant, floatation and product removal, so that the beads used in the invention are re-usable many times over. Useful polymers can be chosen from among the following:

Detailed Description Text (17):

cross-linked ethylene-vinyl acetate copolymers;

Detailed Description Text (20):

cross-linked polymers and copolymers of hydroxyethyl acrylate;

Detailed Description Text (21):

cross-linked polymers and copolymers of hydroxyethyl methacrylate;

Detailed Description Text (22):

cross-linked polymers and copolymers of hydroxyethyl ethacrylate;

Detailed Description Text (23):

cross-linked acrylamide polymers and copolymers;

Detailed Description Text (24):

cross-linked N-substituted acrylamide polymers and copolymers;

Detailed Description Text (25):

cross-linked polymers and copolymers of acrylonitrile; polymethacrylonitrile;

Detailed Description Text (26):

cross-linked ethylene-ethyl acrylate copolymers;

Detailed Description Text (27):

cross-linked ethylene-acrylic acid copolymers;

Detailed Description Text (28):

cross-linked ethylene-methacrylic acid copolymers; polystyrene;

Detailed Description Text (31):

ethylene-propylene copolymers and terpolymers;

Detailed Description Text (32):

cross-linked silicone polymers;

Detailed Description Text (33):

fluorocarbon polymers e.g. polyvinyl fluoride and polyvinylidene fluoride;

Detailed Description Text (37):

polyaminoacids, semicrystalline or cross-linked proteins;

Detailed Description Text (46):

SBR copolymers;

Detailed Description Text (51):

Cross-linked polymers have the additional advantage that they swell to a high degree to provide for ready impregnation with reagents and removal of products.

Detailed Description Text (52):

Preferred polymers for use in the invention have a glass transition temperature below that at which the impregnation and extraction takes place. If the polymer is in its glassy state, i.e. below its glass transition temperature, the diffusion of the chemical into the polymer is hindered, so that impregnation is slowed. Above this temperature, the mobility of the chemical reactants and products is enhanced, leading to shorter impregnation, recovery and reaction times, especially where a bimolecular reaction is to be accomplished.

Detailed Description Text (53):

Specific preferred polymers are cross-linked ethylene-vinyl acetate copolymers.

Detailed Description Text (55):

A specific example of organic chemical synthesis which can be conducted by the process of the present invention is formaldehyde synthesis from carbon monoxide in the presence of water and metal complexes: ##STR1## To conduct this reaction according to the invention, polymer beads are impregnated with carbon monoxide and an appropriate organic soluble metal complex, e.g. ferric carbonyl. Then they are floated on a body of water in exposure to direct sunlight, and formaldehyde and the metal complex catalyst subsequently recovered from the bead. The water reactant can thus derive from the body of water providing floatation. The formaldehyde so formed is useful in a variety of purposes, including conversion to methanol for use as a fuel. This reaction to produce formaldehyde is similar to natural photosynthesis. The choice of polymer in the bead for this reaction is made on the basis of criteria previously discussed--inertness to water, reactants and products, ability to hold but also to release readily the reactants and products and the catalyst or photosensitizer necessary for the reaction, radiation transparency or translucency

etc.

Detailed Description Text (56):

An alternative manner in which the process of the invention may be conducted, in using a gaseous reagent such as carbon monoxide, or in adopting a chemical reaction or compound which is sensitive to oxygen, is to cover the floating beads on the water surface with a solar radiation permeable membrane, under which is provided an atmosphere of reactant or inert gas. The membrane may be supported by the atmosphere of gas beneath it, to exclude oxygen from the vicinity of the impregnated floating beads or provide for their contact with a reactant gas.

Detailed Description Text (63):

Reduction by solar U.V. radiation exposure, of anthraquinone in the polymer layer during the process of this invention, to 9, 10-dihydroxyanthracene, involves the absorption of a specific quantity of energy, known as the reduction potential. The 9, 10-dihydroxyanthracene may then be removed from the polymer bead and subsequent oxidation will yield anthraquinone and energy. The reagent R--OH is normally water, and thus may be supplied by the suspension medium. In the above reaction, the photochemical conversion preferably takes place in the absence of oxygen, so that it is conducted under an inert atmosphere e.g. of nitrogen or CO.sub.2 gas trapped by a solar radiation permeable, gas impermeable blanket. In a subsequent step, the aldehyde is extracted, and the dihydroxyanthracene is treated with oxygen, e.g. while still on the beads, packed into a column. In such treatment, the dihydroxyanthracene is oxidized back to anthraquinone, with generation of useful quantities of hydrogen peroxide. Such a process can advantageously be conducted adjacent to a hydrogen peroxide user, e.g. a pulp and paper facility, since the storage and shipping of hydrogen peroxide is hazardous.

Detailed Description Text (72):

The only commercial method of synthesis of vitamin D is photochemical, the current energy costs for which are substantial. Such a photochemical process is advantageously conducted according to the present invention, since the steroid reactants and products are relatively high molecular weight and hence non-volatile on exposure to sunlight. They are suitably impregnated into and removed from an ethylene-vinyl acetate copolymer as carrier.

Detailed Description Text (76):

Sensitizers used to promote photochemical reaction in the process of the present invention are compounds capable of absorbing solar radiation and transferring it to the reactants, either radiatively or non-radiatively. The appropriate sensitizers may be chemically bound to the polymer layer or to the reactant, but removable from the product after the reaction is complete. They can if desired be left bonded to the polymer beads, if the beads are to be re-used in the same or similar reactions. They can be bound to the polymer in a similar way to that of UV stabilizers commonly used with polymers, or used in other ways analogously to known polymer stabilizer uses.

Detailed Description Text (77):

The types of products which can be synthesized according to the invention, and the reactants which can be used, should have a relatively low vapour pressure in order to be retained in the polymer films for the required exposure times (anywhere from a few hours to, say, one month, depending upon the thickness of the layer and other factors). Where the reactants and/or products are normally unacceptably volatile, they can be introduced into the polymer bead as a complex, which can be made to give up the product/reagent on demand, chemically or thermally. The products and reactants should also be relatively stable to oxygen if they are to be exposed on open bodies of water. Use of beads of the type shown in FIG. 2 can be used in instances of high oxygen sensitivity.

Detailed Description Text (82):

It will be understood that the quinone-hydroquinone reversible redox reaction discussed above is merely a representative example of a redox reaction which can be used for this purpose in the process of the present invention. The system can be generalized, as follows: ##STR6## Reaction (1) takes place in the floating polymer beads, according to the invention, as previously described. A represents any organic compound capable of being photo-reduced in water. It is effectively acting as a chemical "carrier" of hydrogen, for generation and utilization of hydrogen. There are now two alternative reverse reactions to choose: ##STR7## Reaction (2) produces hydrogen fuel which is subsequently used in energy production. Reaction (3) produces electrical energy directly through fuel cell utilization. In either case compound A is regenerated, ready for recycling.

Detailed Description Text (84):

A still further aspect of the present invention concerns nitrogen fixation. The plastic bead or foam system used in the present invention can be used to retain photocatalysts suitable for the fixation of nitrogen from the atmosphere using natural sunlight as the source of energy, to form nitrogenous compounds useful as fertilizers. Such catalysts are normally transition metal catalysts. The nitrogenous compounds are formed in the polymer of the bead itself, and can be recovered therefrom. Alternatively, the beads may be made of a biodegradable polymer, so that the combined beads and nitrogenous product can be utilized as fertilizer.

Detailed Description Text (85):

The economic features of the process of the present invention are highly attractive, in comparison with the capital and energy costs of conventional, silicon-based solar energy collectors and associated convertors. At the current state of the art, silicon solar cells cost about \$100 per square meter of radiation-incident surface, not counting installation, transformer and transmission costs. A one-hectare installation thus costs \$1,000,000. The actual costs of electricity produced from such devices are estimated to exceed 20-50c per kilowatt-hour. In the present invention, 1 kg of polymer will cover 1 square meter of pond surface to a thickness of 1 mm, which at 50c per pound of polymer calculates to a capital cost of about \$10,000 to cover one hectare of water surface. Even at low energy conversion efficiencies, potential economic advantages of the present invention are significant.

Detailed Description Text (88):

Crosslinked ethylene-vinylacetate copolymer beads were prepared by the following procedure. Ethylene-vinylacetate beads (500 g, ELVAX 150) containing approximately 33% vinylacetate ~~were placed in a sealed vessel~~, evacuated and flushed with nitrogen. They were irradiated for three weeks with .gamma.-rays from a cobalt-60 source. The total dose required for crosslinking was about 15 megarad. After .gamma.-irradiation the beads were placed in a Soxhlet extractor and extracted with toluene until no further soluble materials could be recovered. The beads were then dried under vacuum at 40.degree. C. and stored for future use.

Detailed Description Text (98):

Low density polyethylene beads approximately 2 mm in diameter (Tenite 800E) were extracted with 95% ethanol in a Soxhlet extractor and dried. This polymer is non-crosslinked, and has limited crystalline regions 50 g of the beads were placed in a flask with 20 ml 2-undecanone and heated to 60.degree. C. overnight. The amount of 2-undecanone absorbed was determined by extraction of a small sample (2 g) with ethanol followed by G.C. analysis. Samples of the beads were floated on water in a photographic tray and exposed for (1) 28 hrs, and (2) 60 hrs to natural sunlight. A further sample (sample 3) was exposed to a sunlamp for 16 hrs.

CLAIMS:

4. The process of claim 3 wherein said inert carrier is a water buoyant bead

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L2: Entry 9 of 255

File: USPT

Mar 2, 2004

DOCUMENT-IDENTIFIER: US 6699952 B2

TITLE: Modular cytomimetic biomaterials, transport studies, preparation and utilization thereof

Brief Summary Text (9):

Natural membranes are utilized as models for the molecular engineering of membrane-mimetic biosystems because of the potential biological activities associated with natural membranes and their ability to self-organize as non-covalent aggregates. Phospholipids differing in chemical composition, saturation, and size have been utilized as building blocks in the design of structures of complex geometry, including lipid-based cylinders, cubes, and spheres. Surface-coupled bilayers have been produced by assembling a layer of closely packed hydrocarbon chains followed by exposure to either a dilute solution of emulsified lipids or unilamellar lipid vesicles (Spinke et al. [1992] Biophys. J. 63:1667; Florin et al. [1993] Biophys J. 64:375; Seifert et al. [1993] Biophys. J. 64:384). Langmuir-Blodgett techniques have also been used to construct supported bilayers via a process of controlled dipping of a substrate through an organic amphiphilic monolayer (Ulman [1991] An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly, New York: Academic Press). The overall significance of these design strategies lies in the ability to engineer surfaces in which the constituent members can be controlled, modified, and easily assembled with a high level of control over both order and chemistry. Of particular importance is the dialkyl moiety which facilitates the assembly of lipids with dissimilar head groups into surface structures of diverse biomolecular functionality and activity. Nonetheless, limited stability remains the major practical limitation of substrate supported membranes in which the constituent members are associated solely by non-covalent interactions.

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3, 944, 580

comprising a substantially water insoluble, UV-stable polymer, said reactant being supported on the carrier by impregnating the polymer with the reactant.

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